CHAPTER 3

SYNTHESIS OF NANOSTRUCTURED MATERIALS

LEARNING OBJECTIVES

- Introduction, Top-down approach, Bottom-up approach, Photolighography.
- Ball milling, Gas phase condensation, Nonlithographic process.
- Sputtering, Evaporation, Pulsed laser deposition, Chemical vapour deposition.
- Sol-gel technique, Electro deposition, Spray pyrolysis, Collodal synthesis.
- Hydrothermal synthesis, Molecular beam epitaxy,

3.0 INTRODUCTION

Over the last few years a huge array of nano structured materials(NSM) and devices based on metals, metal oxides, ceramics, organic and polymers have been introduced with new functionalities. These materials are known for their unique physical, chemical, optical, electrical, magnetic, thermal and mechanical properties which define them as nanostructures, nanoelectronics, nanobiotechnology etc. In recent years syntesis and studies on nanomaterials and their applications have received wide attention from researchers across various domains. According to the area of application the experimental methodologies are initially optimized for the perfect growth of nanomaterials and for superior material characteristics. These standards are also highly required for nanomaterials which are to be used in nanoelectronics. Some of the essential factors that are to be taken care during fabrication of nanomaterials include their particle size and distribution, shape, crystal structure, composition distribution, purity of nanoparticles, stabilisation of physical properties, high reproducibility mass production and cost effective fabrication.

Nanostructured materials can be fabricated in a numerous ways. Generally to fabricate a nanostructure or nano device, two different approaches are being followed. This includes a number of fabrication stages also. Such routes are commonly known as top-down and bottom-up approaches. In the top-down approach a previously grown perfect material is further processed for the desired function. In the bottom up approach emploitation of material growth is done to obtain the desired size, shape and other characteristics of a nanomaterial.

3.1. TOP-DOWN APPROACH

In top-down approach a bulk material is reduced into constituent nanostructures by suitable processing methodologies. Some of the examples of top-down technique are lithography, etching, ball milling etc. Integrated circuits are manufactured using a sequence of steps such as crystal growth, lithgraphy, etching, ion implantation etc. For the synthesis of nanomaterials ball-milling is an important top-down tehnique where macrocystallne structures are broken down to nanocrystalline structures with the original integrity of material unaltered. This method is also used to prepare nanostructured metal oxides by the chemical reaction between two constituents during crushing. The crystallites are allowed to react with each other by the supplyof kinetic energy during milling process to the required nanostructured metal oxides.

3.2 BOTTOM-UP APPROACH

In bottom-up approach the nanostructures are built from atoms, molecules or atomic clusters through physical and chemical methods. It is clear that in bottom-up technique a nanostructure is constructed block by block in to a larger structure. A nanometric structure is developed into a larger structure through suitable assembling mechanism. During such assemblies the physical forces operating at nanoscale are used to combine basic units into larger structure. Some of the examples of bottom-up technique are sol-gel technique, electrodeposition, physical vapour deposition, chemical vapour deposition, epitaxial growth etc.

The schematic diagram of top-down and bottom-up approaches is shown in Fig-3.2

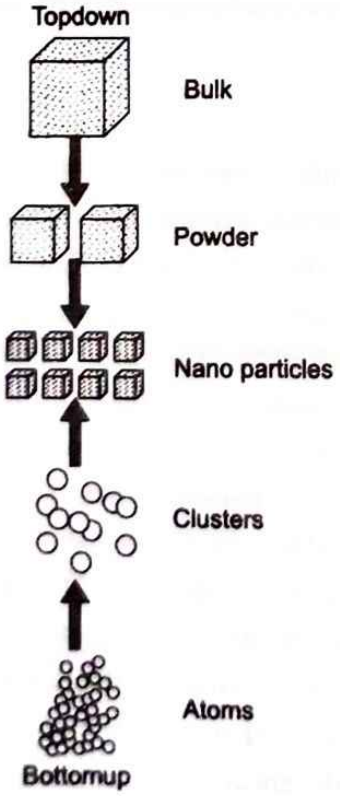


Fig. 3.2 : Schematic of topdown and bottomup approach

3.3 PHOTOLITHOGRAPHY

Lithography is a printing method that uses chemical processes to create an image. Photolithography uses light to transfer a geometric pattern from a photo mask to a light-sensitive chemical (photoresist) on the substrate.

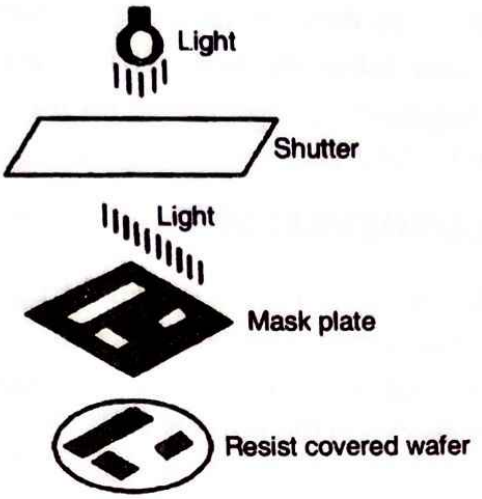


Fig. 3.3 Schematic diagram of photo lithographic fabrication technique

The schematic diagram of photolithographic fabrication technique is shown in the Fig -3.3.

Depending on the pattern on the photomask various nanostructurees can be generated on the substrate which is further used to develop different silicon based photonic and electronic devices.

Limitations

Photolithographic fabrication technique has the following limitations.

(I) Nanostructures less than 100 nm are difficult to be produced due to diffraction effects.

(II) Photolithographic tools are very costly

(III) Implementation is itself a very complex process.

(IV) Perfect alignment between mask and pattern on the wafer is required.

3.4 BALL MILLING

Ball milling is a simple technique for the preparation of nanostructured material. This method is based on the mechanical crushing process. In ball milling method, small balls are allowed to rotate around the inside of a drum and drop with force of gravity on a solid enclosed with the drum. In this way the material is broken down to nanocrystalites. This technique can be readily implemented commercially. The schematic diagram of the functioning of a ball milling technique is shown in Fig-3.4.

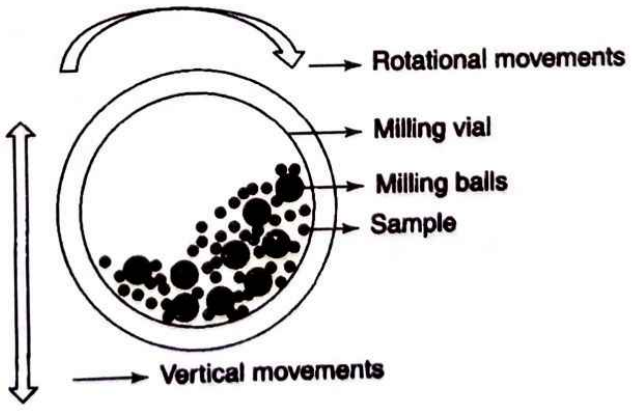


Fig. 3.4 Schematic diagram of the functioning of a ball milling setup

The main objectives of ball milling technique are committed with the particle size reduction, amorphization, tuning the size and shape of the particles, agglomeration and solid state blending. This method can be used ot make a variety of materials such as carbon based materials and nanotubes like carbon nanotubes and born nitride nanotubes, wide range of elimental and oxide powders. The ball milling method is preferred for the synthesis of metal oxides like Al_2O_3, SnO_2, BaT_iO_3 FeO, FeO_3, TiO_2, ZrO_2 etc.

3.5. GAS PHASE CONDENSATION

Gas phase condensation method is one of the most promising method for the production of low cost nanostructured materials. Generally this method is used for the synthesis of single phase metals, semiconductors and metal oxide nanoparticles. The schematic diagram of gas phase condensation method is shown in the Fig-3.5.

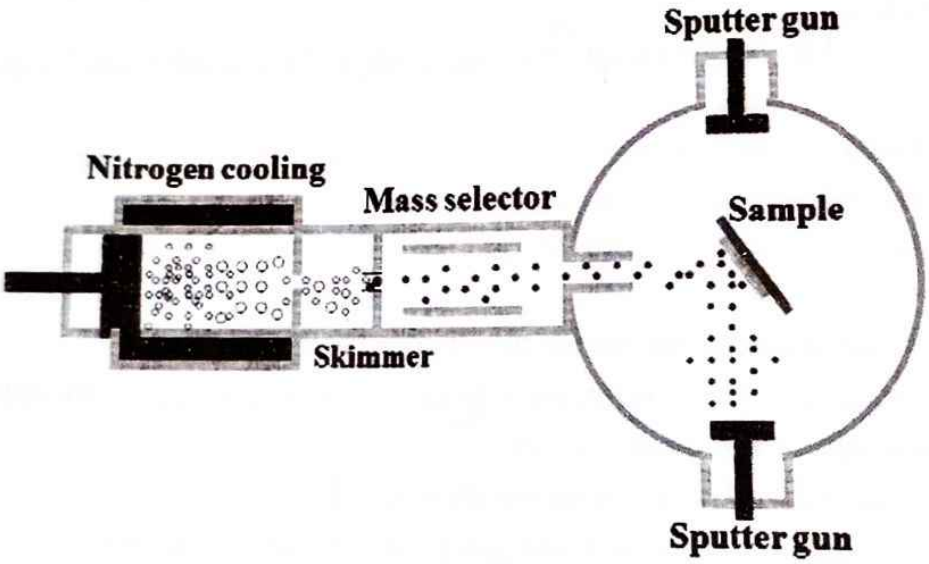


Fig. 3.5 : Schematic diagram of gas phase condensation

Gas phase condensation method is based on nanoparticles generated by evaporation and condensation (nucleation and growth) in a sub-atmospheric inert or reactive gas environment. The generation of atoms clusters by gas condensation proceeds by evaporating a precursor material, either a single component or a compound, in a gas maintained at a low pressure. The evaporated atoms or molecules undergo a homgeneous condensation to form atom clusters through collisions with gas atoms or molecules in the vicinity of a cold surface to condense on it and result in formation of nanoparticles.

3.6. NONLITHOGRAPHIC PROCESS

Nonlithographic process is based on natural self-organization processes. In general nonlithographic methods can be broadly divided into two groups namely (i) vacuum-based deposition process and (ii) solution-based deposition process.

3.6.1 Vaccum-based deposition

In vaccum-based deposition process elements, alloys or compounds are vaporized and deposited under high vaccum (10^{-8} to 10^{-11} mbar). This proces is very clean and the probability of

deposition of foreign and undesired materials is very low. Hence vaccum based deposition techniques are highly favourable for efficient device fabrication. Examples of vaccum-based deposition process are evaporation, sputtering, chemical vapor deposition, laser ablation, molecular beam epitaxy, plasma arc method etc.

Limitations

Vacuum based deposition process has the following limitations -

(i) It requires costly and complicated equipments.

(ii) It requires leak-proof accessories

(iii) It requires vacuum pumps and gauges

3.6.2 Solution -based deposition

Solution based deposition processes are based on chemical reactions in liquid phase. Hence these methods are simple and cost effective. A large range of materials can be synthesized by solution based deposition methods. Examples of solution-based deposition processes are sol-gel, dip-coating, spin-coating spray pyrolyses, electrodeposition, chemical bath deposition etc.

Limitations

Solution-based deposition process has the following limitations -

(i) It is not a very clean process due to the chemical reactions with different constituent materials in solution.

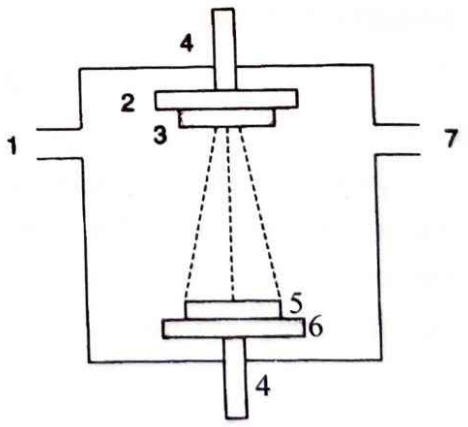
(ii) The desired property is affected due to the presence of undesired molecules,ions inside the synthesized material.

(iii) It is not compatible with the modern solid state device technology which is the primary manufacturing process for electronic and photonic devices.

3.7 SPUTTERING

Sputtering is a common type of physical vapour deposition (PVD) process that is used for thin film deposition. In sputtering atoms in a solid target material are ejected into the gas phase due to bombardment of the material by the energetic ions. The schematic diagram of a sputtering deposition system is shown in Fig-3.7

The sputtering gases are generally selected by considering the atomic weight of the target. Generally neon is preferred for sputtering light elements but krypton or xenon is preferred for sputtering light elements but krypton or xenon is preferred for sputtering heavy elements. Inert gas like argon is preferred as the sputtering as in most of the experiments. Reactive gases are also used in some cases to sputter the desired compounds directly. This method is commonly used in thin-film deposition,



1,7. Gas inlet 2. Target holder
3. Target 4. Heating element
5. Substrate 6. Substrate holding

Fig. 3.7 : Sputtering deposition system

etching and other analytical techniques. Some of the common types of sputtering are DC sputtering, RF sputtering and magnetron sputtering. The sputtering takes place only when the kinetic energy of the incoming particles is much higher than the conventional thermal energies. Similarly the sputtered atoms that are ejected from a target possess a wide energy distribution of the order of tens of eV. These atoms can travel linearly and impact energitically on the substrates or surface of the vacuum chamber. The process parameters must be turned properly otherwise the compound may be formed on the target surface or in flight. A number of other parameters are also available to control the growth and microstructure of a thin film.

Characteristic features of sputtering

Sputtering method has the following characteristic features.

(i) It is a versatile technique to deposit any type of material.

(ii) The properties of synthesized material could be adjusted by varying the experimental conditions.

(iii) It is a simple technology compared to other thin film technologies.

(iv) The use of solid targets ensures the composition of the material to be uniform.

(v) It is an ideal method for depositing metal electrodes for thin-film transistors .

Uses of sputtering

Sputtering method has the following uses

(i) It is extensively used in the fabrication of semiconductor devices and integrated circuits.

(ii) It is used in the fabrication of CDs and DVDs.

(iii) It is used for low-emissivity coating applications in double pane windows.

(iv) It is also used to deposit oxide nitride and carbide thin films.

3.8 EVAPORATION

Evaporation is a common method of thin film deposition where the material to be deposited is heated to high vapour pressure in vacuum. The heating of the material can be done either by electrically resistive heating ie Joule heating or electron bombardment. If the heating is done by Joule heating this the method is thermal evaporation and if the heating is done by electron bombardment this the method is known as e-beam evaporation.

3.8.1 Thermal Evaporation

Thermal evaporation is a method of thin film deposition where the material to be deposited is heated to a high vapour pressure in vacuum by passing high current (10A-100A) through a filament. The schematic diagram of a thermal evaporation system is shown in the Fig-3.8.1.

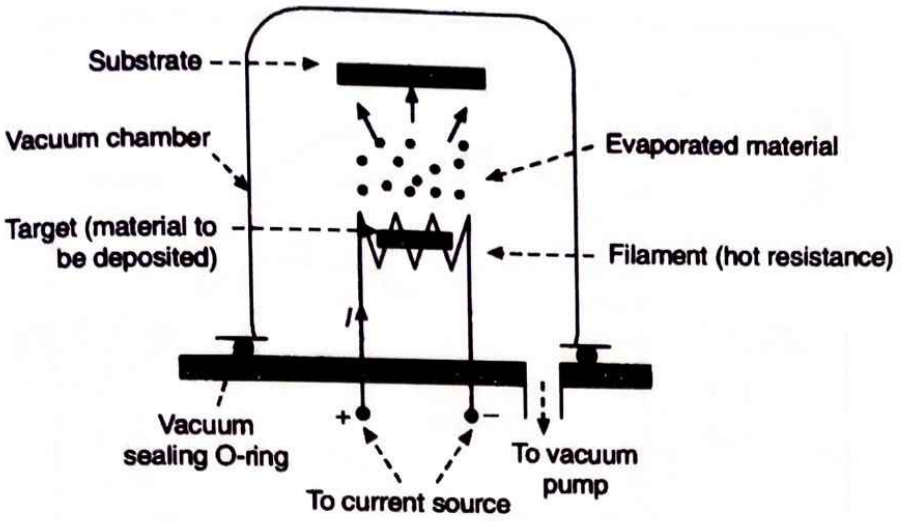


Fig. 3.8.1 Schematic diagram of a thermal evaporation system.

When the material is heated adequately it begins to evaporate and travel through the chamber and deposit on the substrate to be coated. If the vacuum is higher then more efficiently the material will be deposited on the substrate. In a higher vacuum there are small number of molecules in the chamber which will increase the mean free path. A longer mean free path will permit the evaporated molecules to move further before striking an unwanted molecule in the chamber. The rate of deposition of material can be controlled by the current passing through the filament. The evaporation systems are designed by process engineers in accurdance with the demand for the needed gram structure, uniformity, thickness, stress, adhesim strength, optical and electrical properties of the material.

In a typical thermal evaporation system the material to be deposited is loaded into a container called as a crucible which is made up alumina or ceramic materials. The simplest evaporation source is the metal boat which is made up of refractory metals like W, Mo, Ta etc. The substrate is placed above the crucible and the crucible is heated by applying a large current. The material in the crucible starts to vaporize when they are heated. The gaseous atoms travel in straight lines and reach the target and initiate the formation of a thin film. The thickness of the deposited films vary over a few angstroms to microns. Nitrides, oxides, metals and non-metals can be deposited as thin films on the substrates like semiconductor wafers, optical components and solar cells.

3.8.2. E beam evaporation

E-beam evaporation is a method of thin film deposition where the material to be deposited is heated to high vapour pressure in vaccum by the bombardment of high energy electron beam on the material. The high energy electron beam is generated by an electron gun which uses the thermionic emission of electrons produced by an incandescent filament ie cathode. The emitted electrons are accelerated towards an anode by a high potential difference in kilovolt. The material or the crucible or a near perforated disc can be used as the anode. A magnetic field is applied to bend the electron trajectory, allowing the electron gun to be positioned below the evaporation line. The schematic diagram of an E-beam evaporation system is shown in the Fig.3.8.2.

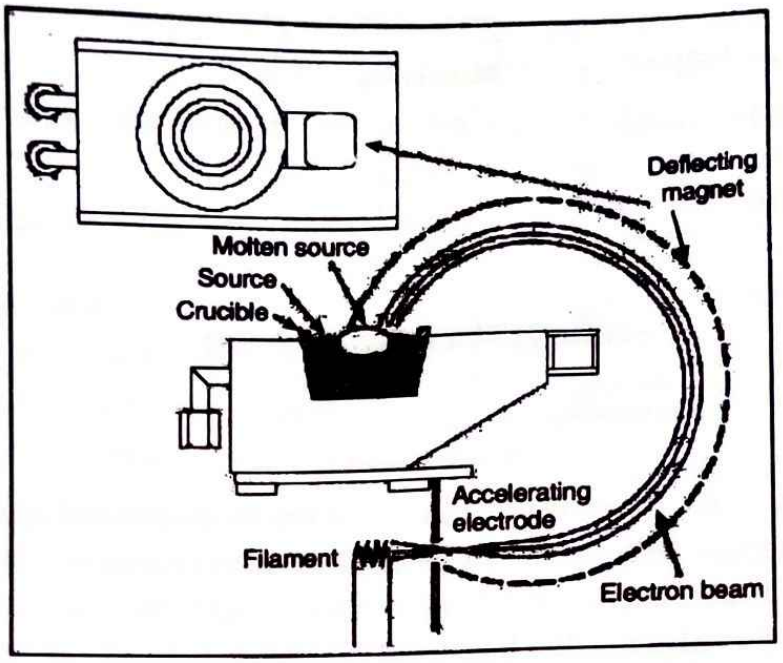


Fig.3.8.2 : Schematic diagram of an e-beam evaporator system.

The energetic impact of the electron beam increases the temperature of the evaporatant creating a hot zone on the material or heated oven in case of an crucible. At a very large temperature the material will begin to evaporate. It is possible to obtain a much localized heating on the material to evaporate with a high density of evaporation powder as the electrons can be localized. This allows the controlling the evaporation rate from low to very high values and it increases the chance of depositing materials with high melting point (W,Ta, C etc). Cooling the crucible avoids the contamination problems from heating and degasification.

3.9. PULSED LASER DEPOSITION

Pulsed laser deposition technique is a method used for thin film deposition as well as synthesis of nanomaterials. In pulsed laser deposition a high power pulsed laser beam is focussed inside a vacuum chamber and allowed to strike the target of the desired material. The intensity of the incident beam vaporizes the target material which gets deposited in the form of thin film on the desired substrate such as silicon. This process can take place in ultra high vacuum or in the presence of same background gases. Some reactive gases such as oxygen and nitrogen are used while gases such as argon are used at some desired pressure to control the deposition rate as well as the film composition. This method has been utilised to fabricate high quality crystalline films. This method was used to deposit a number of materials of complex stoichiometry like piezoelectric materials, ferroelectric materials and superconductors. Multi-element oxides, nitrides, metallic multilayers and various sperlattices also have been deposited successfully by this technique.

The schematic diagram of a PLD system is shown inthe Fig-3.9(a). Laser beam is collimated through lenses to the target for ablation. Target can be rotated. A laser plume is generated between target and the substrate. The substrate can be rotated as well as heated (if needed) for uniform film deposition.

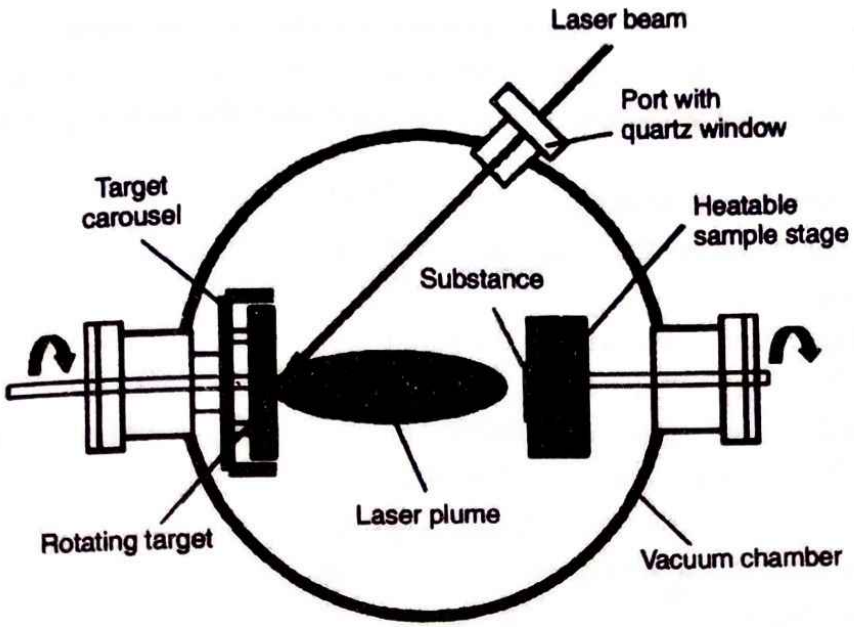


Fig. 3.9(a) : Schematic diagram of a PLD system

The target material which is evaporated by the laser is normally found as a rotating disc attached to a support. However it can also be sintered into a cylindrical rod with rotational motion and a translational up and down movement along its axis of the unique features of PLD lies with the laser source which is held outside the deposition chamber. It relies on a photon interaction to create an ejected plume of materials from any target. This plume (vapour) is collected on a substrate placed at a short distance from the target. Actual physical process of material removal are quite complex and we can consider the ejection of material to occur due to rapid explosion of the target surface due to overheating. The laser induced explosion produces a plume of material with stoichiometry similar to that of target. When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy resulting in evaporation, ablation, plasma formation and even exfoliation. The ejected species expand

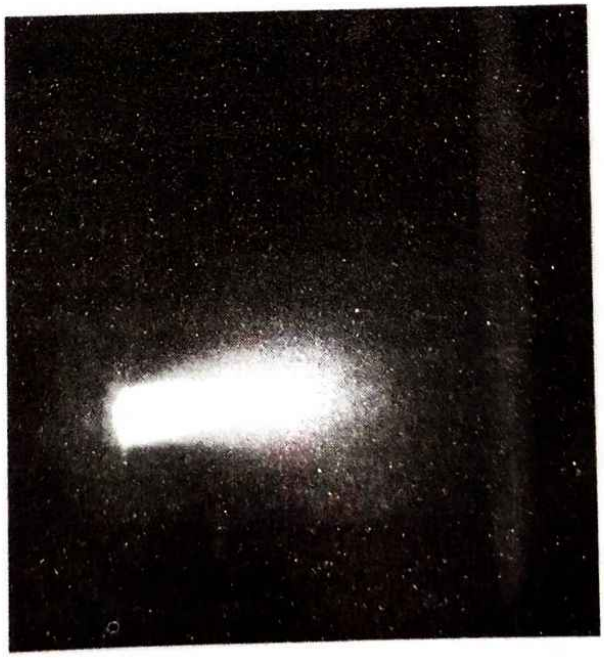


Fig. 3.9(b) Image of a plasma plume generated during a PLD process.

into the vacuum in the form of a plume containing many energetic species incldluing atoms, molecules, electrons, ions, clusters, particulates and molten globules before depositing on the hot substrate. The image of a plasma plume generated during a pulsed laser deposition process is shown in the Fig-3.9(b).

The various stages involved in the process of PLD includes

(i) Laser ablation of the target material and formation of plasma.
(ii) Dynamics of the plasma
(iii) Deposition of the ablated material on the substrate
(iv) Nucleation and growth of the film on the surface of substrate.

The experimental parameters that influence the crystallinity, uniformity, stoichiometry and growth kinetics in a PLD process are given below.

(i) Target material
(ii) Distance from substrate to target
(iii) Pressure in the chamber
(iv) Intensity of laser beam
(v) Ionisation degree of ablated material
(vi) Surface temperature

3.10. CHEMICAL VAPOUR DEPOSITION

Chemical Vapour deposition (CVD) is a chemical process in whcih gaseous molecules are transformed into a solid material in the form 0D, 1D, 2D and 3D nanostructured materials on the surface of a substrate. This process is used to produce high-purity, high perfrmance solid materials. This technique is also used in the semiconductor industry to produce thin films. CVD method is widely used in micro and nano-fabrication process such as carbon fibres, carbon nano-fibres, carbon nano-filaments, carbon nano-tubes, carbon nano-rods, SiO_2, Silicon-germanium, tungsten, silicun carbine nanostructures silicon nitride nanomaterials, silicon oxynitride and titanium nitride. This process is also used to produce synthetic diamonds and nano-diamonds.

The schematic diagram of a CVD is shown in the Fig-3.10(a). Chemial vapour deposition is a sequential process whcih starts from initial vapour phase, progresses through a series of sub-processes and culminates in the formation of solid thin-film of the final nano-structure.

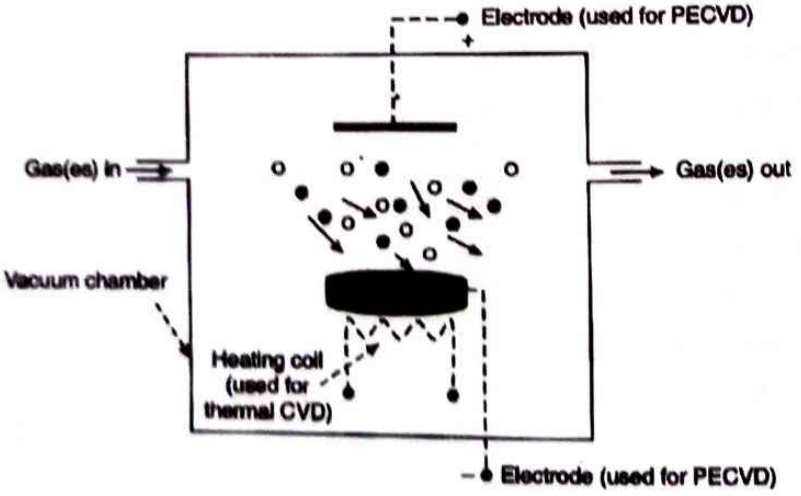


Fig. 3.10(a) Schematic diagram of a CVD system. A heating coil is used for thermal CVD and electrodes are used for plasma enhanced (PE) CVD.

This process consists of the following five steps.

(i) A predefined mix of reactant gases and diluent inert gases are placed into the CVD chamber by the mass flow controller at a specified flow rate.

(ii) The gas species move to the surface site.

(iii) The reactants get absorbed on the surface site.

(iv) The reactants undergo chemical reactions with the substrate to form the nanostructured materials.

(v) The gaseous reaction products are desorbed and evacuated from the CVD chamber.

The schematic diagram of various processes involved in CVD is shown in Fig-3.10(b).

According to operating pressure, CVD can be classified as :

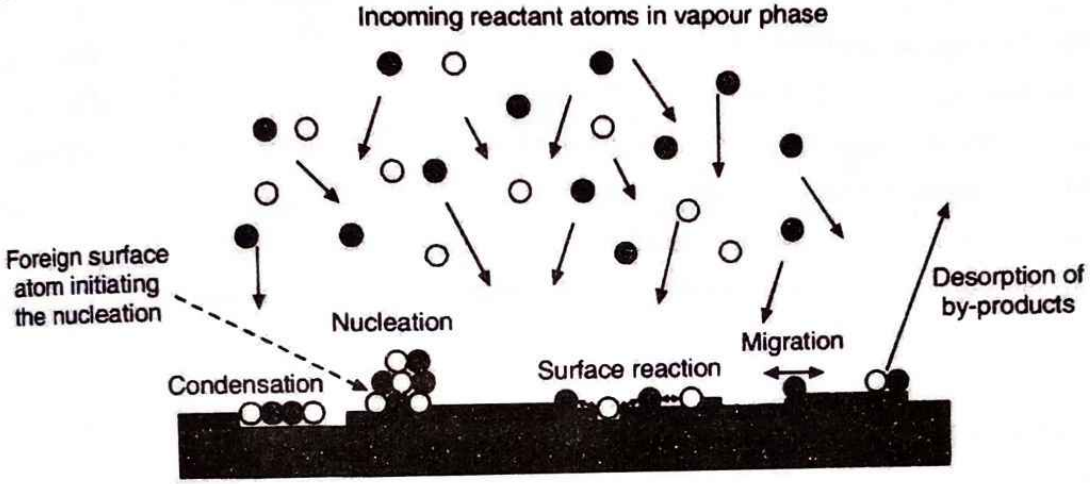


Fig. 3.10(b) Schematic diagram of various processes involved in CVD.

(i) **APCVD** - APCVD is atmospheric pressure CVD and in this case CVD process takes place at atmospheric pressure.

(ii) **LPCVD** - LPCVD means low pressure CVD and here CVD occurs at subatmospheric pressures. Reduce pressure causes reduction of unwanted gas, phase reactions and improve film uniformity across the wafer.

(iii) **UHVCVD** - UHVCVD means ultraligh vacuum CVD and in this case CVD process takes place at a very low pressure below 10^{-6} Pa.

According to the physical characterstics of the vapour us :d, CVD can be classified as -

(i) **AACVD** – AACVD means aerosol assisted CVD and here the precursors are transported to the substrate by means of a liquid/gas aerosol which can be generated ultrasonically. This method is best suited for use with involatile precursors.

(ii) **DLICVD** – DLICVD means direct liquid injection CVD and in this case the precursors are in liquid form and liquid solutions are injected in a vaporization chamber towards injectors and then the vapours are transported to the substrate. This method is suitable for use on liquid or solid precursors.

(iii) **MOCVD** – MOCVD means metal organic CVD and here the precursors are metal organic precursors which are used to deposit thin films. This method is used to deposit a wide variety of materials.

According to the source of energy, CVD process can be classified as -

(i) **PECVD** – PECVD means plasma enhanced CVD and here a plasma is created to enhance chemical reaction rates of the precursors. This method is used to generate high quality and aligned carbon nanotubes (CNT), nano-diamond films and many other nano materials.

(ii) **HFCVD** – HFCVD means hot filament CVD and here a hot filament is used to supply the required energy to chemically decompose source gases. This method is used to deposit CNT, nano-diamond and many other nano materials.

(iii) **RTCVD** – RTVVD means rapid thermal CVD and here heating lamps are used to rapidly heat the surface of substrate so that heating only takes place at the substrate rather than at the gas or walls of the unwanted gas-phase reactions that can lead to particle formation.

3.11 SOL-GEL TECHNIQUE

Sol-gel technique is a wet chemical synthesis which is used for the fabrication of colloidal dispersions of inorganic and organic-inorganic hybrid materials. This process involves the evalution of networks through the formation of a colloidal suspenson (sol) and gelation of the sol to form a network in a continuous liquid phase. The precursors used for synthesizing the colloids consist of metallic ions and ligands which are elements surrounded by various reactive species. Metal alkoxides (aluminates, titanates, borates and cuprates) and alkoxysilanes (tetramethoxy silane i.e TMOS, tetraethoxy sialane i.e TEOS) are most popular because they react readily with water. In general sol-gel formation occurs in four steps.

(i) Hydrolysis and alcoholysis

$$M-OR + H_2O \xrightarrow{\text{Hydrolysis}} M-OH + R-OH$$

$$M-O-M + R-OH \xrightarrow{\text{Alcoholysis}} M-OR + M-OH$$

(ii) Water and alcohol condensation and polymerisation of monomors to form particles.

$$M-OH + M-OH \xrightarrow{\text{Water condensation}} M-O-M + H_2O$$

$$M-OR + M-OH \xrightarrow{\text{Alcohol condensation}} M-O-M + R-OH$$

(iii) Growth of particles

(iv) Agglomeration of networks throughout the liquid medium resulting in thik gel.

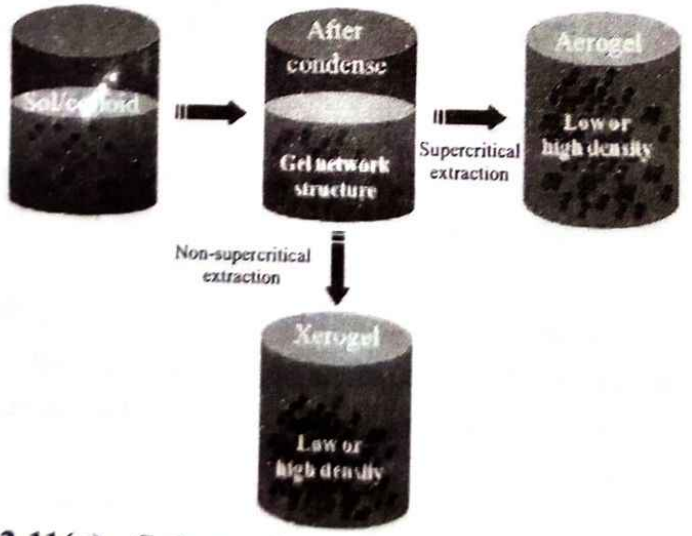


Fig. 3.11(a) : Schematic diagram for sol-gel process

The basic scheme for the sol-gel process is shown in the Fig-3.11(a). Sol-gel process is used for the preparation of nanomaterials in the form of nano-particles, nanofibres, nanoftlms, aerogels and nanoporoces materials. This method is also used to deposit thin film on various substrates via dip-coating or spin-coating or spray-coating process. For sol-gel dip-coating process the substrate is dipped into the sol and taken out to coat it with the required materials. For sol-gel spin-coating process, the sol is dropped by some arrangements like syringe to the substrate followed by spinning of the substrate. For sol-gel spray-coating process the sol is sprayed on the substrate to get a uniform coating and then heated to get the desired film. The schemate diagram of sol-get dip-coating/spin-coating/spray coating process is shown in the Fig-3.11(b)

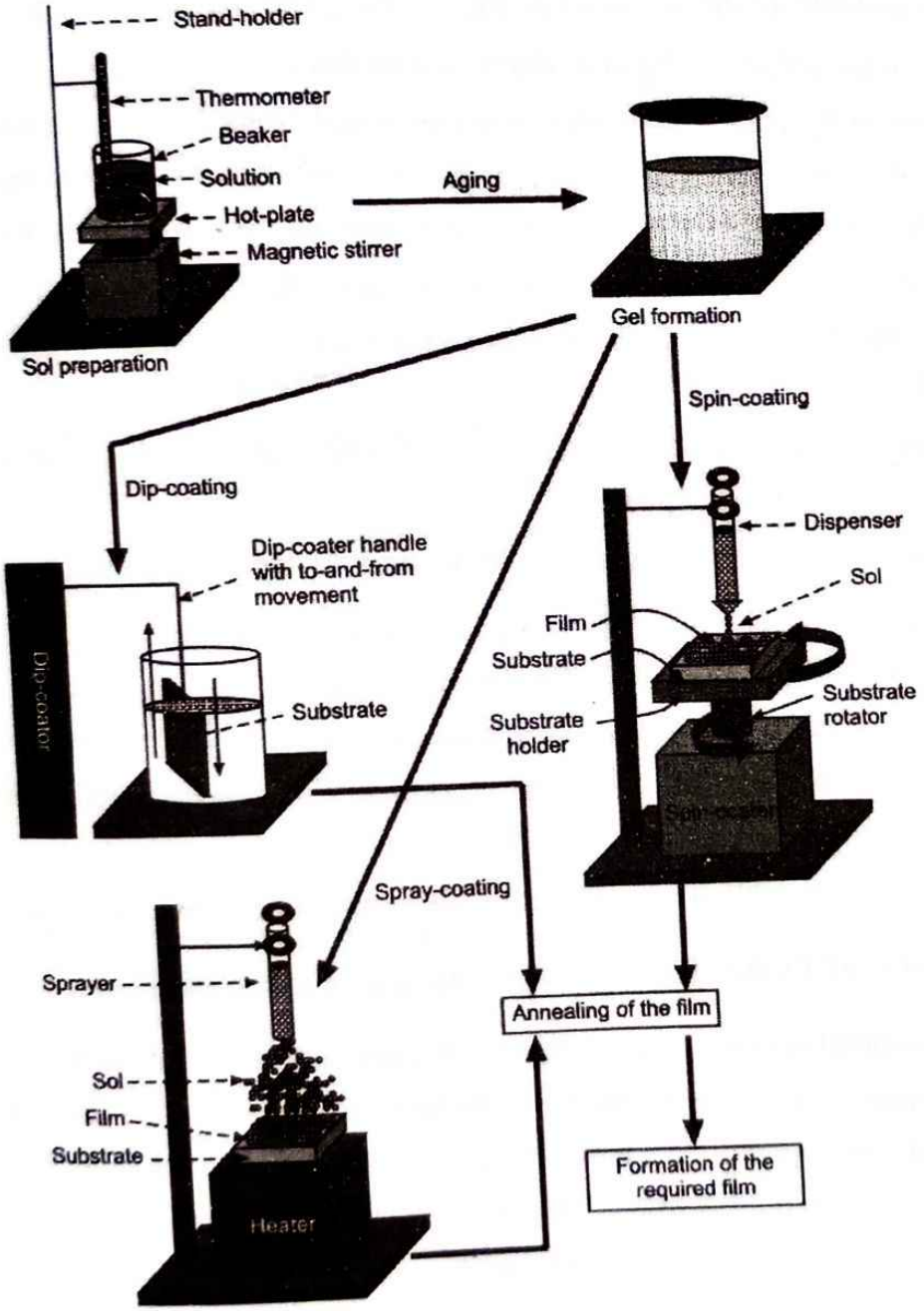


Fig.3.11(b) Schematic diagram of sol–gel dip-coating/spin-coating/spray-coating process to deposit micro/nanocrystalline thin film.

Advantages

Sol-gel process has the following advantages

(i) It is a very simple technique because this process is based on chemical reactions in liquid phase

(ii) It is cost effective because very simple accessories are required for the chemical reaction and deposition of materials.

(iii) It is suitable for the synthesis of nanocomposites.

(iv) It is also suitable for the synthesis of organic-inorganic hybrid materials.

(v) A large range of materials can be deposited by this process.

(vi) This process is versatile enough to produce a large number of materials such as aerogel, xerogel, ceramic materials, micro powder, nano powder, nanostructured thin films, nano particles, nano wires, nano rods, nano pillars, because the deposition is done in liquid phase

(vii) This process has precise control over the doping level.

(viii) This process also has precise control over phase and chemical constituents in the materials prepared.

(ix) Large and complex shaped substrates can also be coated by sol-gel process because the deposition is done in liquid phase.

(x) Possibility of high purity of starting material can be achieved in sol-gel method.

Limitations.

Sol-gel process has the following limitations :

(i) It is not a very clean process because the process involves chemical reactions.

(ii) The process contains undesired atoms, molecules, ions in the materials, which deteriorates the electrical and optical properties of material deposited.

(iii) This process is not compatible with the modern solid state fabrication techique.

3.12 ELECTRO DEPOSITION

Electrodeposition is a liquid based deposition technique where an electric current is passed through a polar liquid by applying electric potential between two electrodes. Due to the application of electrical energy the liquid breaks into ions and other charged compounds and these charged materials are deposited on the electrodes. Hence thin layers of films of some desired materials can be coated on the substrate by suitable arrangements of preferred substrates on the electrodes. The schematic diagram of an electrodeposition system is shown in the Fig - 3.12.

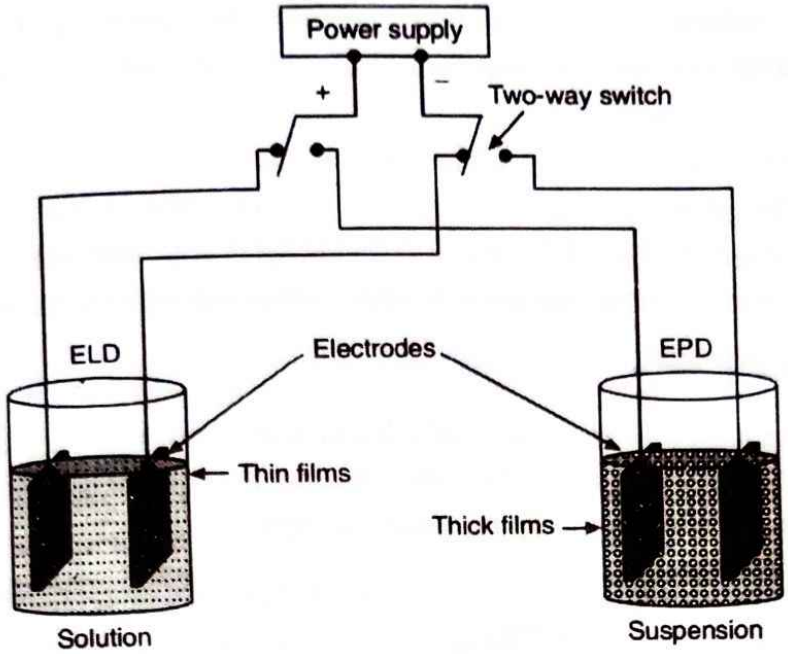


Fig. 3.12 Schematic diagram of electrodeposition apparatus.

This method is used to make electroplated materials which is an electrodeposition process to coat a conductive object with a thin layer of metal. The primary application of electroplating is the deposition of a layer of metal having some desired property of abrasion, wear resistance, corrosion protection, lubricity improvement of aesthetic qualities etc onto a surface lacking that property. Another application of electroplating is to build up thickness on undersized parts. This method is also used in ceramic processing.

There are two types of Electrodeposition process use in celamic processing. These are electrophoretic deposition (EPD) and electrolytic deposition (ELD). EPD is a cathodic electrodeposition process in which suspensions of ceramic particles are used. ELD is based on the use of metal salts solutions. ELD enables the formation thin ceramic films and nanostructured poweders. EPD is an important tool in the preparation of thik ceramic films and body shaping. Electrodeposition process is termed as aniodisation because the pores are formed in the anode of an electrodeposition cell. The dimensions of the pores depend on various factors such as electrolyte, aniodization current, aniodizatin time, deposition temperature etc.

Advantages

Electro deposition process has the following advantages

(i) It provides rigid control of thickness of film, uniformity and deposition rate.

(ii) It is attractive due its low equipment cost and starting materials.

(iii) It is suitable for the formation of uniform of uniform films on substrates of complicated shapes, impregnation of porous substrates and deposition on selected areas of the substrates, due to the application of electric field.

(iv) The amount of material deposited can be controlled by controlling the number of charged particles transferred because the material deposition in electrodeposition follows Faraday's laws.

(v) This process is very useful in nanofabrication process

(vi) It is also useful in the fabrication of self assembled and organized nano-porous material such as aniodic aluminium oxide(AAO) which is known as porous alumina and porous silicon (PS) and growth of nano- particles, nano-rods, nano-wires through the nano-pores.

3.13 SPRAY PYROLYSIS

Spray pyrolysis is a solution process in which nanoparticles are directly deposited by spraying a solution on a heated substrate surface, where the constituents react to form a chemical compound. The schematic diagram of a spray pyrolysis system is shown in the Fig-3.13.

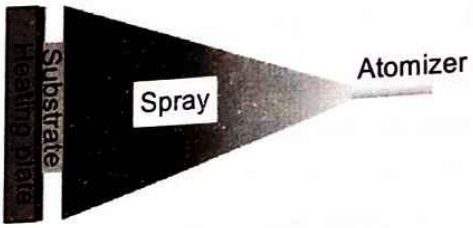


Fig. 3.13 : Schematic diagram of spray pyrolysis system

The chemical reactants are selected such that the products other than the desired compund are volatile at the temperature of deposition. The spray pyrolysis represents a very simple and relatively cost effective method, because the equipments are cheap, as compared to other film deposition methods. It provids an extremely easy technique for preparing fims of any composition and does not require high quality substrates, chemicals, expensive vacuum apparatus and exotic gases. Spray pyrolysis system consists of an atomizer, pre-cursor solution, substrate heater and temperature controller. Various types of atomizers are usually used in spray pyrolysis method, such as air blast atomizer, ultrasonic atomizer and electrostatic atomizer. In air blast atomizer the liquid is exposed to a stream of air. In ultrasonic atomizer the ultrasonic frequencies produce the short wavelengths necessary for fire atomization. In electrostatic atomizer the liquid is exposd to a high electric field.

3.14. COLLODAL SYNTHESIS

Colloidal method is a simple and well established wet chemical precipitation process in which solutions of the different ions are mixed under controlled temperature and pressure to form insoluble precipitates.

For metal nanoparticles the basic principles of colloidal methods of prepation were known since antiquity e.g. gold colloids used for high quality red and purple stained glass from medieval times to date. However proper scientific investigations of colloidal methods started in 1857 when Faraday has published results of his experiments with gold. He prepared gold colloids by reduction of $HAuCl_4$ with phosphorous. Now colloidal processes are widely used to produce nanomaterials such as metals, metal oxides, organics and pharmaceuticals.

In colloidal methods, nanomaterials are prepared by performing certain chemical reactions using appropriate precursor chemicals in colloidal media. The reactions are carried out in water or alcohol media where solutions of different ions are mixed under controlled temperature and pressure to form insoluble precipitates. There are two different methods for the synthesis of nanomaterials through colloidal synthesis. The first one is the size selective precipitation method which is based on the size dependent solubility of nanomaterials in specific solvent. The second one is uniform particle size distribution method by performing fast nucleating reactions.

Advantages.

Colloidal method has the following advantages.

(i) It is a very simple method and the reaction takes place at low temperature.
(ii) It ensures morphological control and size selective growth.
(iii) It helps to control the particle size from a very smal level.
(iv) It ensures cost effective and large scale production of nanomaterials.
(v) In this method mono dispersed particles with ultra high purity can be established.

Limitations

Colloidal method has the following limitations.

(i) It possesses low stability.
(ii) The organic stabilizers complicate the structure and properties of the whole system.

3.15. HYDROTHERMAL SYNTHESIS

In hydrothermal synthesis homogeneous or heterogeneous reaction takes place in the presence of aqueous solvents under high temperature and pressure to produce solid products which are insoluble under ordinary conditions. This method is used in the synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The schematic diagram of a hydrothermal system is shown in the Fig-3.15.

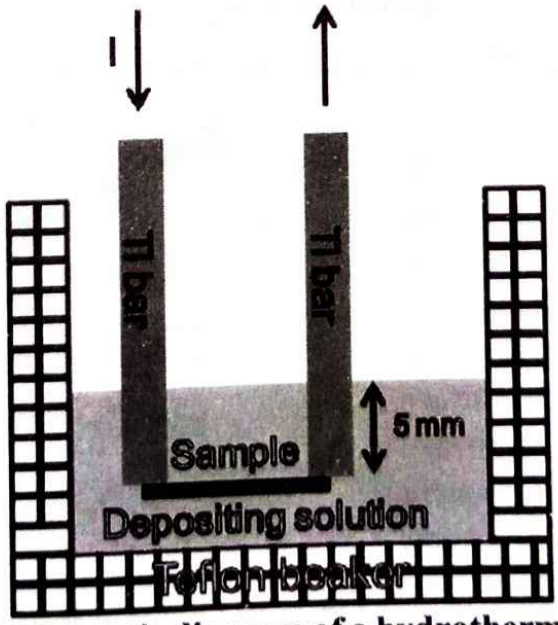


Fig. 3.15 : Schematic diagram of a hydrothermal system

The precursor materials are dissolved in water (solvent) and transferred into a stainless steel vessel called as autoclave. When the transfer process is completed the autoclave is sealed tightly and subjected to thermal treatments. The temperature is fixed over 80 to 250°C for the synthesis of simple nanostructures. At these high temperatures, the supercritical solvent reacts on the precursor materials to result the product formation. Surfactants are also involved in such reactions along with the precursor materials to procure a nanostructure with a desired morphology. Some of the common surfactants are tributylamine, triethylamine, triethanolamine, cyclohexyamine, ammonium chloride, hexamethylenetetramine, ethylene glycal and ethanolamine. The supercritical solvents can also be used in the extraction, chemical manufacturing, waste treatment, recycling etc.

Advantages

Hydrothermal synthesis has the following advantages.

(i) It is simple and cost effective.

(ii) It provides a higher diffusivity, lower viscsity, higher dissolving power for the efficient synthesis of nano materials.

(iii) It provide higher reaction rate through accelerated interaction between precursors.

(iv) It is used to prepare a variety of nanostructures with effective shape control.

(v) It facilitates low temperature operation in the presence of appropriate solvents.

(vi) It can be used to process pure phase and homogeneous materials.

(viii) It can also be used to process the desired materials having desired characteristcs.

(viii) It facilitates the fabrication of complex materials, with a higher dispersion rate.

(ix) The reaction kinetics of this process can be enhanced through nucleation control.

Disadvantages.

Hydrothermal synthesis has the following disadvantages.

(i) It requires expensive autoclaves.

(ii) It is impossible to observe the grown of cystal.

3.16. MOLECULAR BEAM EPITAXY

Molecular beam epitaxy (MBE) is a technique used for the epitaxial growth of materials by means of chemical interaction of one of the several molecular beams of different intensities and compositions that occur on the surface of a heated single crystalline substrate. This method is an ultra high vacuum (UHV) - based technique for preparing high quality epitaxial structures with monlayer control.

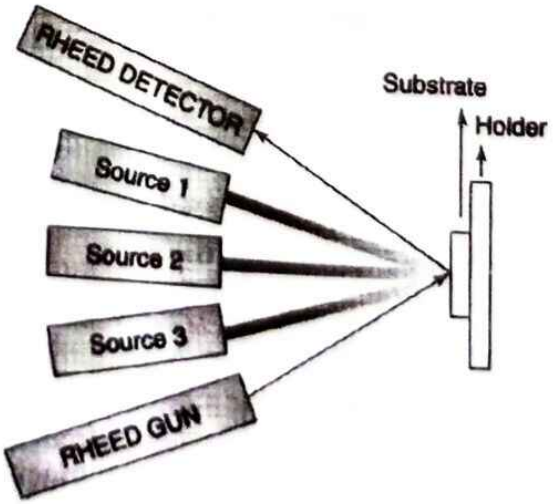


Fig. 3.16 : Schematic diagram of a MBE system.

The schematic diagram of a molecular beam epitaxy (MBE) system is shown in the Fig.3.16. This technique has precise control over beam fluxes by using collimated beams and rapid flux swithcing. This method also ensures a presice control over the growth conditions to ensure high purity materials deposits. This technique also enables the real time monitoring and control of film growth to ensure best conditions of stoichiometry and epitaxy. In a typical solid source MBE system, the ultra-pure form of precursor materials are heated in separate quasi-Kundsen effusion cells, where they start to sublime slowly. The gaseous elements travel in the form of a beam which is composed of evaporated molecules and reach the wafer. The gaseous elements condense on the wafer as deposits where they may react with each other or with other reactants to form the desired products. The molecular beam can be referred as the unidirectional kinematic flow of molecules without any resistance and epitaxy refers to the ordered growth of one crystalline layer on another crystaline layer. The ultra-high vacuum chambers connected with the growth chamber are maintained by a system made up of cryopumps and cryopanels. The function of cryopumps and cryopanels is to cool the substrates once the reaction is completed. The cryogenic temperatures also act as a sink to store the impurities under vaccum conditions. Hence the vaccum levels are held high to obtain high quality films. The substrates are placed on a mount that can be heated up to several hundred degrees celcius during deposition. Reflection high energy electron diffraction (RHEED) techniques are used to monitor the growth of material during their MBE deposition. Computer controlled shutters are used to control the thickness of the deposits precisely to a single layer of the atoms. These arrangements enable the intricate structures of the layers of different materials to be deposited more conveniently. The electron confined structures such as quantum dots and quantum wells can be developed more readily by MBE technique. This method is used to produce highly complex systems and structures of varying layers that can be processed for a wide range of electronic and optoelectronic applications like high speed transistors, light emitting diodes, solar cells and solid state lasers.

The salient features of an MBE system are

(i) It has the potential to fabricate atomically abrupt hetcrojunction and maintain the desired doping levels in only material.

(ii) The ability to produce a desired composition in a material possessing very high electron mobility has enabled the fabrication of high performance devices through MBE system.

(iii) It offers the possibility to integrate optically active materials on heterostructure devices to foresel high speed digital and optical circuit related applications.

(iv) It provides low growth rate.

(v) It provides low growth temperature.

(vi) It provides smooth growth surface in atomic steps.

(vii) It provides precise control of surface composition and morphology.

(viii) It provides abrupt variation of chemical composition at interfaces.

SUMMARY

- The essential factors that are to be taken care during fabrication of nanomaterials include their particle size and distribution, shape, crystal structure, composition distribution, purity of nanoparticles, stabilisation of physical properties, high reproducibility mass production and cost effective fabrication.
- In the top-down approach a previously grown perfect material is further processed for the desired function.
- In the bottom up approach emploitation of material growth is done to obtain the desired size, shape and other characteristics of a nanomaterial.
- In top-down approach a bulk material is reduced into constituent nanostructures by suitable processing methodologies.
- In bottom-up approach the nanostructures are built from atoms, molecules or atomic clusters through physical and chemical methods.
- Lithography is a printing method that uses chemical processes to create an image.
- Photolithography uses light to transfer a geometric pattern from a photo mask to a light-sensitive chemical (photoresist) on the substrate.
- In ball milling method, small balls are allowed to rotate around the inside of a drum and drop with force of gravity on a solid enclosed with the drum.
- The main objectives of ball milling technique are committed with the particle size reduction, amorphization, tuning the size and shape of the particles, agglomeration and solid state blending.
- Gas phase condensation method is based on nanoparticles generated by evaporation and condensation (nucleation and growth) in a sub-atmospheric inert or reactive gas environment.
- Nonlithographic process is based on natural self-organization processes.
- In vaccum-based deposition process elements, alloys or compounds are vaporized and deposited under high vaccum (10^{-8} to 10^{-11} mbar).
- Vaccum based deposition techniques are highly favourable for efficient device fabrication.
- It requires costly and complicated equipments. It requires leak-proof accessories. It requires vacuum pumps and gauges.
- Solution based deposition processes are based on chemical reactions in liquid phase.
- Photolithographic tools are very costly
- It is not a very clean process due to the chemical reactions with different constituent materials in solution.
- It is not compatible with the modern solid state device technology which is the primary manufacturing process for electronic and photonic devices.
- Sputtering is a common type of physical vapour deposition (PVD) process that is used for thin film deposition.
- In sputtering atoms in a solid target material are ejected into the gas phase due to bombardment of the material by the energetic ions.

- The sputtering gases are generally selected by considering the atomic weight of the target.
- Sputtering is a versatile technique to deposit any type of material.
- Sputtering is an ideal method for depositing metal electrodes for thin-film transistors .
- Sputtering is extensively used in the fabrication of semiconductor devices and integrated circuits.
- Sputtering is used for low-emissivity coating applications in double pane windows.
- Evaporation is a common method of thin film deposition where the material to be deposited is heated to high vapour pressure in vacuum.
- If the heating is done by Joule heating this the method is thermal evaporation.
- If the heating is done by electron bombardment this the method is known as e-beam evaporation.
- Thermal evaporation is a method of thin film deposition where the material to be deposited is heated to a high vapour pressure in vacuum by passing high current (10A-100A) through a filament.
- E-beam evaporation is a method of thin film deposition where the material to be deposited is heated to high vapour pressure in vaccum by the bombardment of high energy electron beam on the material.
- Pulsed laser deposition technique is a method used for thin film deposition as well as synthesis of nanomaterials.
- In pulsed laser deposition a high power pulsed laser beam is focussed inside a vacuum chamber and allowed to strike the target of the desired material.
- Chemical Vapour deposition (CVD) is a chemical process in whcih gaseous molecules are transformed into a solid material in the form 0D, 1D, 2D and 3D nanostructured materials on the surface of a substrate.
- APCVD is atmospheric pressure CVD and in this case CVD process takes place at atmospheric pressure.
- LPCVD means low pressure CVD and here CVD occurs at subatmospheric pressures.
- UHVCVD means ultraligh vacuum CVD and in this case CVD process takes place at a very low pressure below 10^{-6} Pa.
- AACVD means aerosol assisted CVD and here the precursors are transported to the substrate by means of a liquid/gas aerosol which can be generated ultrasonically.
- DLICVD means direct liquid injection CVD and in this case the precursors are in liquid form and liquid solutions are injected in a vaporization chamber towards injectors and then the vapours are transported to the substrate.
- MOCVD means metal organic CVD and here the precursors are metal organic precursors which are used to deposit thin films.
- PECVD means plasma enhanced CVD and here a plasma is created to enhance chemical reaction rates of the precursors.

- HFCVD means hot filament CVD and here a hot filament is used to supply the required energy to chemically decompose source gases.
- RTVVD means rapid thermal CVD and here heating lamps are used to rapidly heat the surface of substrate so that heating only takes place at the substrate rather than at the gas or walls of the unwanted gas-phase reactions that can lead to particle formation.
- Sol-gel technique is a wet chemical synthesis which is used for the fabrication of colloidal dispersions of inorganic and organic-inorganic hybrid materials.
- Sol-gel technique is suitable for the synthesis of nanocomposites.
- This process is versatile enough to produce a large number of materials such as aerogel, xerogel, ceramic materials, micro powder, nano powder, nanostructured thin films, nano particles, nano wires, nano rods, nano pillars, because the deposition is done in liquid phase
- Large and complex shaped substrates can also be coated by sol-gel process because the deposition is done in liquid phase.
- Possibility of high purity of starting material can be achieved in sol-gel method.
- Electrodeposition is a liquid based deposition technique where an electric current is passed through a polar liquid by applying electric potential between two electrodes.EPD is a cathodic electrodeposition process in which suspensions of ceramic particles are used.
- ELD is based on the use of metal salts solutions.
- ELD enables the formation thin ceramic films and nanostructured poweders.
- Electrodeposition process is termed as aniodisation because the pores are formed in the anode of an electrodeposition cell.
- Electrodeposition provides rigid control of thickness of film, uniformity and deposition rate.
- Electrodeposition is attractive due its low equipment cost and starting materials.
- Electrodeposition is suitable for the formation of uniform of uniform films on substrates of complicated shapes, impregnation of porous substrates and deposition on selected areas of the substrates, due to the application of electric field.
- Electrodeposition process is very useful in nanofabrication process
- Electrodeposition is also useful in the fabrication of self assembled and organized nano-porous material such as aniodic aluminium oxide(AAO) which is known as porous alumina and porous silicon (PS) and growth of nano- particles, nano-rods, nano-wires through the nano-pores.
- Spray pyrolysis is a solution process in which nanoparticles are directly deposited by spraying a solution on a heated substrate surface, where the constituents react to form a chemical compound.
- Colloidal method is a simple and well established wet chemical precipitation process in which solutions of the different ions are mixed under controlled temperature and pressure to form insoluble precipitates.

- Colloidal method is a very simple method and the reaction takes place at low temperature.
- Colloidal method ensures morphological control and size selective growth.
- In colloidal method mono dispersed particles with ultra high purity can be established.
- In hydrothermal synthesis homogeneous or heterogeneous reaction takes place in the presence of aqueous solvents under high temperature and pressure to produce solid products which are insoluble under ordinary conditions.
- Hydrothermal synthesis provides a higher diffusivity, lower viscsity, higher dissolving power for the efficient synthesis of nano materials.
- Hydrothermal synthesis facilitates low temperature operation in the presence of appropriate solvents.
- Hydrothermal synthesis facilitates the fabrication of complex materials, with a higher dispersion rate.
- Hydrothermal synthesis requires expensive autoclaves.
- Molecular beam epitaxy (MBE) is a technique used for the epitaxial growth of materials by means of chemical interaction of one of the several molecular beams of different intensities and compositions that occur on the surface of a heated single crystalline substrate.
- Molecular beam epitaxy has the potential to fabricate atomically abrupt hetcrojunction and maintain the desired doping levels in only material.
- The ability to produce a desired composition in a material possessing very high electron mobility has enabled the fabrication of high performance devices through MBE system.
- Molecular beam epitaxy offers the possibility to integrate optically active materials on heterostructure devices to foresel high speed digital and optical circuit related applications.
- Molecular beam epitaxy provides low growth rate.
- Molecular beam epitaxy provides precise control of surface composition and morphology.
- Molecular beam epitaxy provides abrupt variation of chemical composition at interfaces.

QUESTIONS

Long Answer Type Questions :

1. Discuss about the top-down technique for the synthesis of nanomaterials.
2. Explain about the bottom-up technique for the synthesis of nanostructured materials.
2. What do you mean by photolighography ? Write its limitations.
4. Write short notes on :
   (a) Ball milling (b) Gas phase condensation
5. What is vacuum based deposition ? Write its limitations.
6. What do you mean by solution based deposition ? Write its limitations.
7. What do you mean by sputtering ? Write the characteristics of sputtering and give its uses.
8. What do you mean by evaporation technique ?

9. Discuss about the thermal eaporation method of thin film deposition.
10. Explain about the E-beam evaporation technique of thin film deposition.
11. Write short notes on :
    (a) Pulsed laser deposition
    (b) Chemical vapour deposition
12. Discuss about the classification of chemical vapour deposition process.
13. What do you mean by sol-gel technique?
    Explain in details and write the advantages and limitations of this technique.
14. Explain about electrodeposition technique. Write its advantages.
15. Discuss about the spray pyrolysis method for the synthesis of nanomaterials.
16. Explain about the colloidal synthesis and write its advantages and limitation.
17. Write whort notes on :
    (a) Hydrothermal synthesis
    (b) Molecular beam epitaxy
18. What is difference between physical vapour deposition and chemical vapour deposition ?
19. What is dip-coating ?
20. What is spin- coating ?
21. What is spray-coating ?

Very Short Answer Type Questions :

1. Write examples of top-down approach.
2. Write examples of bottom-up approach.
3. Which method uses chemical processes to create an image ?
4. Which method uses light to transfer a geometric pattern from a photo mask to a light sensitive chemical on the substrate ?
5. Which method is based on the mechanical crushing process ?
6. Which method requires perfect alignment between mask and pattern on the wafer ?
7. Which method is used for the synthesis of single phase metals, semiconductors and metal oxide nanoparticles ?
8. Which process is based on natural self organisation processes ?
9. Which method requires leak-proof accessories ?
10. Which method requires vacuum pumps and gauges ?
11. Which method is not compatible with the modern solid state device technology ?
12. Which method is used in the fabrication of CDs and DVDs ?
13. In which method the material to be deposited in heated to high vapour pressure in vacuum ?
14. In which method the heating is done by Joule heating ?
15. In which method of heating is done by electron bombardment ?

16. Which method is uses for thin film deposition as well as synthesis of nano-materials ?
17. Which method is used to produce high purity and high performance solid materials ?
18. What is APCVD ?
19. What is LPCVD ?
20. What is UHVCVD ?
21. Classify CVD process according to the physical characteristics of the vapour used.
22. Classify CVD process according to the source of energy.
23. Which method is used for the fabrication of colloidal dispersions of inorganic and organic - inorganic hybrid materials ?
24. Which method has precise control over doping level ?
25. In which method an electric current is passed through a polar liquid by applying electric field between two electrodes ?
26. Which method is useful in the fabrication of self-assembled and organised nano-porous material such as aniodic aluminium oxide and porous silicon and growth of nano-particles, nanorods, nano-wire through the nanopores ?
27. In which method nano-particles are directly deposited by spraying a solution on a heated substrate surface where the constituents react to form a chemical compound ?
28. In which method solutions of the different ions are mixed under controlled temperature and pressure to form insoluble precipitates ?
29. In which method homogeneous or heterogeneous reaction takes place in the presence of aqueous solvents under high temperature and pressure to produce solid products ?
30. Which method requires extensive autoclaves ?
31. What is electrophoretic deposition ?
32. What is electrolytic deposition ?
33. Which technique is used for the epitaxial growth of materials by means of chemical interaction of one of the several molecular beams of different intensities and compositions that occur on the surface of a heated single crystalline substrate ?
34. Which technique has the potential to fabricate atomically abrupt heterojunction and maintain the desired doping levels in any material ?
35. Which technique provides abrupt variation of chemical composition at the interfaces ?